



TITLE:

<Division of Synthetic Chemistry>Structural Organic Chemistry

AUTHOR(S):

CITATION:

<Division of Synthetic Chemistry>Structural Organic Chemistry. ICR Annual Report 2017, 24: 6-7

ISSUE DATE:

2017

URL:

<http://hdl.handle.net/2433/230237>

RIGHT:

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Division of Synthetic Chemistry

– Structural Organic Chemistry –

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Scope of Research

Fundamental studies are being conducted for the creation of new functional π -systems with novel structures and properties, and for evaluation of their application as organic semi-conducting materials for photovoltaic and electroluminescent devices. The major subjects are: 1) organochemical transformation of fullerenes C_{60} and C_{70} , specifically organic synthesis of endohedral fullerenes by the technique of molecular surgery; 2) generation of ionic fullerene species and their application for the synthesis of functional material; 3) synthesis of new carbon-rich materials by the use of transition metal complex; and 4) creation of new functional π -materials with unique photoelectric properties.

KEYWORDS

π -Conjugated Systems
Endohedral Fullerenes
Functional Materials
Perovskite-Based Solar Cells
Organic Solar Cells



Selected Publications

Shimogawa, H.; Yoshikawa, O.; Aramaki, Y.; Murata, M.; Wakamiya, A.; Murata, Y., 4,7-Bis[3-(dimesitylboryl)thien-2-yl]benzothiazazole: Solvato-, Thermo-, and Mechanochromism Based on the Reversible Formation of an Intramolecular B-N Bond, *Chem. Eur. J.*, **23**, 3784-3791 (2017).
Futagoishi, T.; Aharen, T.; Kato, T.; Kato, A.; Ihara, T.; Tada, T.; Murata, M.; Wakamiya, A.; Kageyama, H.; Kanemitsu, Y.; Murata, Y., A Stable, Soluble, and Crystalline Supramolecular System with a Triplet Ground State, *Angew. Chem. Int. Ed.*, **56**, 4261-4265 (2017).
Chaolumen; Murata, M.; Wakamiya, A.; Murata, Y., Unsymmetric Twofold Scholl Cyclization of 5,11-Dinaphthyltetracene: Selective Formation of Pentagonal and Hexagonal Rings via a Dication Pathway, *Angew. Chem. Int. Ed.*, **56**, 5082-5086 (2017).
Nakamura, T.; Okazaki, S.; Arakawa, N.; Satou, M.; Endo, M.; Murata, Y.; Wakamiya, A., Synthesis of Azole-fused Benzothiadiazoles as Key Units for Functional π -Conjugated Compounds, *J. Photopolym. Sci. Technol.*, **30**, 561-568 (2017).
Ozaki, M.; Katsuki, Y.; Liu, J.; Handa, T.; Nishikubo, R.; Yakumaru, S.; Hashikawa, Y.; Murata, Y.; Saito, T.; Shimakawa, Y.; Kanemitsu, Y.; Saeki, A.; Wakamiya, A., Solvent-Coordinated Tin Halide Complexes as Purified Precursors for Tin-based Perovskites, *ACS Omega*, **2**, 7016-7021 (2017).
Hashikawa, Y.; Murata, M.; Wakamiya, A.; Murata, Y., Palladium-Catalyzed Cyclization: Regioselectivity and Structure of Arene-Fused C_{60} Derivatives, *J. Am. Chem. Soc.*, **139**, 16350-16358 (2017).

Palladium-Catalyzed Cyclization: Regioselectivity and Structure of Arene-Fused C₆₀ Derivatives

The palladium-catalyzed cyclization on the fullerene C₆₀ cage has been achieved using several aryl halides and C₆₀. This reaction was found to be accelerated by the addition of pivalic acid, which can be rationally explained by the computational study based on the concerted metalation-deprotonation mechanism. We have also demonstrated the regioselective π -functionalization using pre-functionalized molecules possessing the same substructure on the C₆₀ cage. The single crystal X-ray analysis and electrostatic potential map revealed that the orientation of entrapped H₂O inside the naphthalene-fused open-cage C₆₀ derivative is electrostatically demanded due to the naphthalene-fusion and construction of the opening.

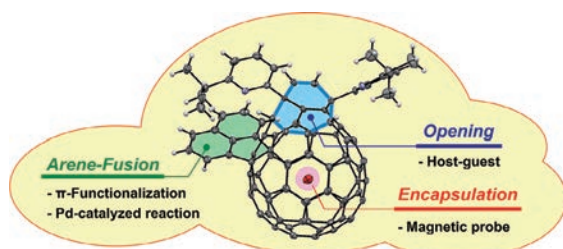


Figure 1. Regioselective naphthalene-fusion on the open-cage C₆₀ derivative.

Synthesis of Azole-fused Benzothiadiazoles as Key Units for Functional π -Conjugated Compounds

2,1,3-Benzothiadiazole (BT) is a widely used electron-accepting unit in organic electronics including organic solar cells. As modifications of BT skeleton, two types of azole-fused BT units were designed and synthesized; thiazole-fused BT with an electron-withdrawing C=N bond and imidazole-fused BT with an electron-donating nitrogen atom as well as an electron-withdrawing C=N bond. Ele-

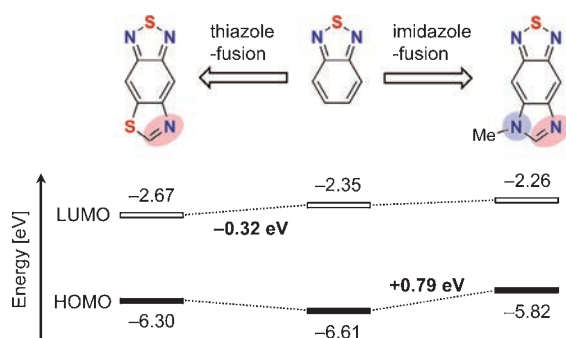


Figure 2. Effect of azole-fusion on the electronic structure of BT skeleton. Calculated at B3LYP/6-31G(d) level of theory.

ctrochemical measurements and theoretical calculations suggest that thiazole-fusion enhances the electron-accepting ability, whereas imidazole-fusion endows the BT skeleton with electron-donating ability while maintaining its electron-accepting ability. Moreover, in thiazole-fused BT units, the electronic structure could be further modulated by varying the oxidation state of the sulfur atom in methylthio group at the fused thiazole ring.

Solvent-Coordinated Tin Halide Complexes as Purified Precursors for Tin-Based Perovskites

A series of solvent-coordinated tin halide complexes was prepared as impurity-free precursors for tin halide perovskites, and their structures were determined by single-crystal X-ray diffraction analysis. Using these precursors, the tin halide perovskites (MASnI₃ and FASnI₃) were prepared, and their electronic structures and photophysical properties were examined under inert conditions by means of photoelectron yield spectroscopy as well as absorption and fluorescence spectroscopies. Their valence bands (MASnI₃: -5.02 eV; FASnI₃: -5.16 eV) are significantly higher than those of MAPbI₃ or the typical hole-transporting materials 2,2',7,7'-tetrakis(*N,N*-di-*p*-methoxyphenylamino)-9,9'-spirobifluorene and poly(bis(4-phenyl)(2,4,6-trimethylphenyl)amine). These results suggest that to develop the solar cells using these tin halide perovskites with efficient hole-collection properties, hole-transporting materials should be chosen that have the highest occupied molecular orbital levels higher than -5.0 eV.

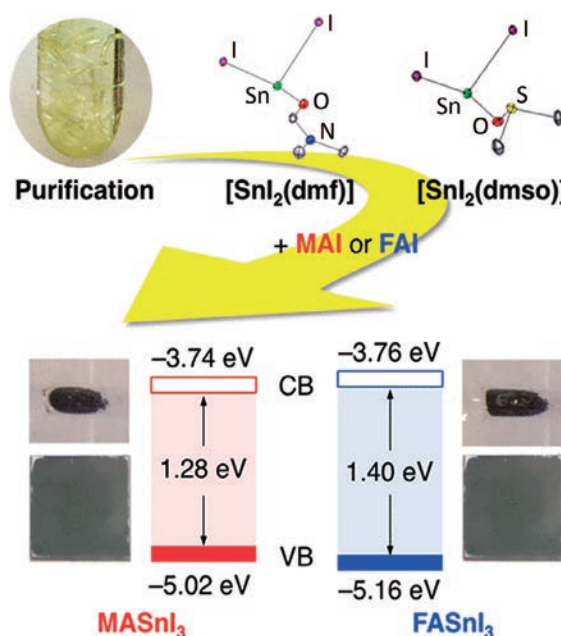


Figure 3. Valence and conduction bands of Sn-based perovskites prepared from purified precursor materials.